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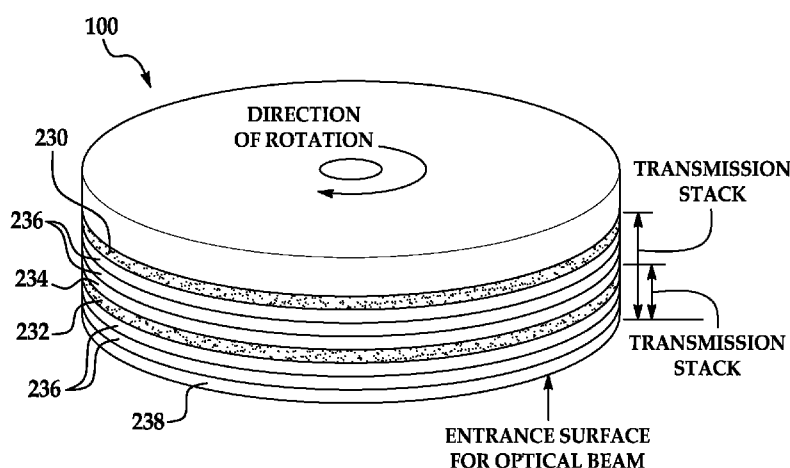


FIG. 5

(57) Abstract: An optical data recording medium (100) includes a substrate (220) and a markable coating including first and second layers (230, 232). The first layer (230) of the markable coating is established on the substrate (220) and includes a first predetermined ratio of a first absorber dye (239) and a first contrast-forming agent (240). The second layer (232) of the markable coating is established on the first layer (230) of the markable coating and includes a second predetermined ratio of a second absorber dye (239') and a second contrast-forming agent (240'). The second predetermined ratio is different from the first predetermined ratio.



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10 OPTICAL DATA RECORDING MEDIUM INCLUDING
A MULTI-LAYERED MARKABLE COATING

BACKGROUND

The present disclosure relates generally to an optical data recording medium including a multi-layered markable coating.

15 Materials that produce color and/or contrast change upon stimulation with radiation are used in optical recording and imaging media and devices. Further, widespread adoption of and rapid advances in technologies relating to optical recording and imaging media have created a desire for greatly increased data storage capacity in such media. Thus, optical storage technology has evolved from
20 the compact disc (CD) and laser disc (LD) to far denser data types such as digital versatile disc (DVD) and blue laser formats such as BLU-RAY and high-density DVD (HD-DVD). "BLU-RAY" and the BLU-RAY Disc logo mark are trademarks of the BLU-RAY Disc Founders, which consists of 13 companies in Japan, Korea, Europe, and the U.S.

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BRIEF DESCRIPTION OF THE DRAWINGS

Features and advantages of embodiments of the present disclosure will become apparent by reference to the following detailed description and drawings, in which like reference numerals correspond to similar, though perhaps not
30 identical, components. For the sake of brevity, reference numerals or features having a previously described function may or may not be described in connection with other drawings in which they appear.

Figs. 1A and 1B are absorbance graphs respectively depicting the dependence of the initial absorption of a coating on the amount of absorber used (Fig. 1A), and the dependence of the final contrast of a coating on the amount of contrast-forming agent used (Fig. 1B);

5 Fig. 2 is a flow diagram depicting an embodiment of a method for making an embodiment of an optical data recording medium;

Fig. 3 is a semi-schematic perspective view and block diagram illustrating an embodiment of an optical disc recording system;

10 Fig. 4 is a schematic cross-sectional view of an embodiment of a recording medium shown in conjunction with a partial block diagram of some of the elements of the system represented in Fig. 3;

Fig. 5 is a perspective view of another embodiment of a recording medium; and

15 Fig. 6 is a graph illustrating example HF signals received from elements of a photo detector when reading an embodiment of the optical disc.

DETAILED DESCRIPTION

Embodiments of the medium disclosed herein advantageously include a markable coating including multiple layers for forming optically detectable marks. Each of the layers includes a respective predetermined ratio of absorber to contrast forming agent. The absorber within each layer may be individually configured such that each layer exhibits a different sensitivity (i.e., intensity of absorption at a particular wavelength or power (mW) needed to write to the layer). Furthermore, the contrast agent within each layer may be configured such that the resulting intensities of marks are distinguishable from one layer to the next.

25 Still further, the sensitivity of the individual layers may be tuned substantially independently of the final contrast of the respective layers. This concept is illustrated in Figs. 1A and 1B. Fig. 1A illustrates an absorbance graph of marked (i.e., optically detectable marks are formed in the recording layer) and unmarked recording media having different amounts of absorber in the recording layer (in this

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instance, the absorber is S0512, a cyanine absorber which is available from Few Chemicals GmbH, Germany). As depicted, both the marked and unmarked recording media including 120 mg of the absorber have a more intense absorbance than the recording media with less or no absorber. Fig. 1B illustrates an absorbance graph illustrating the difference in absorbance between respective marked and unmarked recording media having different amounts of contrast-forming agent (in this instance, the contrast-forming agent is JM42B, a curcumin derivative available from Hewlett-Packard Co., Palo Alto, CA) therein. The difference in the contrast of the media with more contrast-forming agent is greater than the difference in the contrast of the media with less contrast-forming agent. These results illustrate that the amount of absorber may be selected independently of the amount of contrast-forming agent, that the amount of absorber will not significantly or deleteriously affect the resulting contrast, and that the amount of contrast-forming agent will not significantly or deleteriously affect the initial absorbance.

Multi-layered coatings have been particularly difficult to achieve in one-component or one-function systems, in part because in such systems the contrast after writing is completely dependant on the initial parameters and concentration of the single component or of the mixture of single function components.

Certain terms are used throughout the following description and claims that refer to particular system components. As one skilled in the art will appreciate, various companies may refer to a particular component by different names. This document does not intend to distinguish between components that differ in name but not function.

Reference is made herein to BLU-RAY technologies. Disc specifications for BLU-RAY discs currently include the following: wavelength = 405 nm; numerical aperture (NA) = 0.85; disc diameter = 12 cm; disc thickness = 1.2 mm; and data capacity $\geq 23.3/25/27$ GB. BLU-RAY discs are currently used to store 2 hours of high resolution video images or 13 hours of conventional video images. A blue-violet laser having a wavelength between 380 nm and 420 nm, and particularly 405

nm is used as the light source for BLU-RAY discs. Another technology using blue light (380 nm ~ 420 nm radiation) is HD-DVD.

As used herein, the terms “wavelength”, “wave band”, “absorption band” or “band” refer to light frequencies, radiation, and/or absorption ± 30 nm from the stated value. For example, the 405 nm band includes wavelengths ranging from 375 nm to 435 nm, and the 650 nm band includes wavelengths ranging from 620 nm to 680 nm. Furthermore, the term “light” includes electromagnetic radiation of any wavelength or band and from any source.

As used herein, the terms “color agent”, “contrast agent” and “contrast-forming agent” are defined as any material that, in conjunction with an absorber will produce contrast in the desired read band due to physical or chemical changes. The contrast agent may be a leuco dye, a combination of a leuco dye and a developer/developer precursor, or another material that undergoes changes in absorption coefficient (k), changes in refractive index (n), changes in reflectivity (r), changes in coating dimension (e.g., thickness), or distortion.

“Leuco dye”, as used herein, refers to a color- or contrast-forming substance that is colorless or exhibits one contrast in a non-activated state and that produces or changes contrast in an activated state. As used herein, the terms “developer” and “activator” describe a substance that reacts with the dye and causes the dye to alter its chemical structure and change or acquire color.

The term “absorber”, as used herein, describes a substance that absorbs a predetermined wavelength or range of wavelengths and transfers the absorbed energy to the contrast agent, thereby causing the contrast agent to alter its chemical and/or physical structure and produce an optically detectable change.

Referring now to Fig. 2, an embodiment of the method of making an embodiment of the optical data recording medium (depicted as reference numeral 100 in Figs. 3-5) is depicted. Generally, the method includes establishing first and second layers of a markable coating on a substrate, the first layer including a first predetermined ratio of a first absorber dye and a first contrast-forming agent, and the second layer including a second predetermined ratio of a second absorber dye

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and a second contrast-forming agent; and tuning at least one of the first predetermined ratio or the second predetermined ratio such that i) the first and second absorbers exhibit different intensities of absorbance at a predetermined wavelength, and ii) an optically detectable mark formed in the first layer exhibits a different contrast than an optically detectable mark formed in the second layer. It is to be understood that the optical data recording medium and the method of making the same are further discussed in reference to Figs. 3-5.

The optical data recording medium 100 disclosed herein may be used to record optical data or visual images, which then transmit readable patterns when exposed to light beams of a predetermined wavelength. The system used to write and/or read such data is shown in Fig. 3 and includes optical components 148, a light source 150 that produces an incident energy beam 152, a return beam 154 which is detected by a pickup 157, and a transmitted beam 156. In the transmissive form, the transmitted beam 156 is detected by a top detector 158 (a non-limiting example of which is a photo detector) via lens or optical system 600, and is also analyzed for the presence of signal agents. It is to be understood that Fig. 3 shows an abbreviated block diagram of the read/write system 170 illustrating some of the same optical components shown in Fig. 3.

Fig. 3 also illustrates a drive motor 162 and a controller 164 for controlling the rotation of the optical disc/imaging medium 100 (also referred to herein as recording medium 100). Mark(s) (shown as 242, 242' in Fig. 3) may be read/detected by an optical sensor (e.g., optical pickup 157). The sensor (e.g., optical pickup 157) is positioned so as to detect at least one readable pattern of the optically detectable mark(s) 242, 242' on the imaging medium 100. Generally, the sensor is configured so that a laser focuses on a plane of the first layer (shown as 230 in Fig. 4) or the second layer (shown as 232 in Fig. 4), depending on which pattern of mark(s) 242, 242' is to be read. It is to be understood that the pattern of the marks 242 in the underlying layer 230 may be read through the overlying layer 232, in part because the contrast of the marks 242' is darker than the contrast of the layer 232 (discussed further hereinbelow). The sensor reads one or more

readable patterns as the imaging medium 100 moves in relation to the sensor. The sensor may send the readable pattern(s) in the form of one or more signals to a processor 166.

The processor 166 and an analyzer 168 may be implemented together or in the alternative for processing the return beam 154 with a signal 165 from the pickup 157 to the processor 166, as well as processing a transmitted beam 156 from a signal 163 transmitted from the optical detector 158 and associated with the transmissive format. A display monitor 114 is also provided for displaying the results (generally in the form of data) of the processing. The system may also include a computer data base (not shown) which collects and stores the processed/analyzed data for subsequent retrieval.

As previously mentioned, Fig. 4 shows an abbreviated block diagram of the read/write system 170 illustrating some of the same optical components shown in Fig. 3. Specifically, Fig. 4 illustrates the read/write system 170 applying an incident energy beam 152 onto the first layer 230 of the recording medium 100.

The recording medium 100 includes a substrate 220 and the markable coating (i.e., marking layer), which includes layers 230, 232, established on a surface 222 thereof. In one embodiment (as shown in Fig. 4), the first layer 230 is established directly adjacent the substrate 220, and the second layer 232 is established directly adjacent the first layer 230. In another embodiment (as shown in Fig. 5), the first layer 230 is established directly adjacent the substrate 220, a spacer layer 234 is established between the first and second layers 230, 232, and a cover or protective layer 238 is established between the second layer 232 and the optical beam. Such protective layers 238 are generally known and enable writing to and reading of the layers 230, 232 while protecting such layers from scratching, dirt, etc. It is to be understood that other embodiments, such as that depicted in Fig. 4, of the imaging medium 100 do not include a protective layer 238.

In still other embodiments (also shown in Fig. 5), buffer layers 236 may be established adjacent the respective layers 230, 232 such that each is positioned on a surface of the respective layer 230, 232 that is first exposed to the optical beam.

Non-limiting examples of suitable buffer layers 236 include dielectric materials that enable the desirable wavelength(s) to be transmitted therethrough. It is to be understood that additional buffer layers 236 may be included, as shown in Fig. 5.

The layers 230, 232, 234, 236, 238 may be established via any desirable
5 technique, including, but not limited to rolling, spin-coating, spraying, lithography, or screen printing.

The substrate 220 for the imaging/recording medium 100 may be any substrate upon which it is desirable to make a mark 242, 242' such as, for example, the polymeric substrate used in conventional CD-R/RW/ROM,
10 DVD±R/RW/ROM, HD-DVD or BLU-RAY disc. Substrates suitable for Ultra Density Optical (UDO) discs may also be used. The substrate 220 may also be paper (e.g., labels, tickets, receipts, or stationery), an overhead transparency, or another surface upon which it is desirable to provide marks 242, 242'.

In many embodiments, it may be desirable to provide layers 230, 232 that
15 have a respective thickness less than 100 nm. In order to achieve this, spin coating is one suitable application technique. In addition, it may be desirable to provide marking compositions that are capable of forming layers 230, 232 that are each equal to or less than 100 nm thick. In such cases, the marking layers 230, 232 should be, *inter alia*, free from particles that would prevent formation of such a
20 layer, i.e., free from particles having a dimension greater than 100 nm. In some instances, the components of the respective layers 230, 232 may be in complete solution, thereby producing molecular level film aggregates.

Furthermore, in many applications it may be desirable to provide markable layers 230, 232 that are transparent. In such a case, any particles present in the
25 layers 230, 232 would have an average size less than half of the wavelength of the light to which the layers 230, 232 are transparent. While layers 230, 232 in which all particles are smaller than 200 nm would serve this purpose, it may be more desirable to utilize layers 230, 232 in which the marking components are dissolved, as opposed to one in which they are present as particles. Still further, as target
30 data densities increase, the dot size, or mark size, that can be used for data

recording decreases. Some currently available technologies require an average dot size of 200 nm or less. For all of these reasons, layers 230, 232 are therefore desirably entirely free of particles that are larger than half the wavelength of the write radiation.

5 Both the first and second layers 230, 232 include an absorber dye 239, 239' and a contrast agent 240, 240' in respective predetermined ratios. It is to be understood that by altering/tuning the ratio of the materials, it is possible to alter the optical properties (e.g., sensitivity and contrast) of the respective layers 230, 232. As such, the ratio of absorber dye 239, 239' to contrast agent 240, 240' in each
10 layer 230, 232 is determined, at least in part, so that the respective layers 230, 232 exhibit a desirable sensitivity at a predetermined wavelength, and the marks 242, 242' formed in the respective layers 230, 232 exhibit a desirable contrast. The ratios of the layers 230, 232 are different if it is desirable that i) the second layer 232 be more sensitive than the first layer 230 (i.e., less power is needed to write to
15 the second layer 232 than is needed to write to the first layer 230), for example, when the layers 230, 232 are to be independently marked, and ii) the contrast exhibited by the marks 242 formed in the first layer 230 be darker than the marks 242' formed in the second layer 232. Generally, the layer 230 furthest from the surface entrance for the optical beam (see, e.g., Fig. 5) requires more energy since
20 the total energy delivered is marking energy, and some of the energy is absorbed by the outer layer 232.

Furthermore, the sensitivity of the respective layers 230, 232 may be altered substantially independently of the final contrast of the respective layers 230, 232. Obtaining a desirable sensitivity may be accomplished by altering the concentration
25 of the absorber 239, 239' in the respective predetermined ratio. The final contrast of the respective layers 230, 232 may be tuned by altering the concentration of and/or material(s) selected for the contrast agent 240, 240' in the respective predetermined ratio.

In one embodiment, the predetermined ratio of the materials in the first layer
30 230 is selected to obtain an optical density difference (between marked and

unmarked regions of the layer 230) ranging from about 0.15 to about 0.20, and the predetermined ratio of the materials in the second layer 232 is selected to obtain an optical density difference (between marked and unmarked regions of the layer 232) ranging from about 0.2 to about 0.4. The optical density differences for the layers 230, 232 may be determined using the previously described range of absorbance values for absorbers 239, 239' and contrast formers 240, 240'.

The absorber dye 239, 239' and the contrast agent 240, 240' of each layer 230, 232 may be suspended or dissolved or finely dispersed in a matrix or binder (e.g., a polymeric matrix including, for example, polyacrylates, polystyrenes, polyalkenes, or polycarbonates). In some instances, the contrast agent 240, 240' and the absorber dye 239, 239' are completely soluble in the coating matrix or binder. In one embodiment, the layers 230, 232 also include a fixing agent (not shown).

In the embodiments disclosed herein, the matrix material can be any composition suitable for dissolving and/or dispersing the absorber 239, 239' and the contrast agent 240, 240'. Acceptable matrix materials include, but are not limited to, UV-curable matrices such as acrylate derivatives, oligomers and monomers, with or without a photo package. A photo package may include a light-absorbing species which initiates reactions for curing the matrix, such as, for example, benzophenone derivatives. Other examples of photoinitiators for free radical polymerization monomers and pre-polymers include, but are not limited to, thioxanethone derivatives, anthraquinone derivatives, acetophenones and benzoin ether types. It may be desirable to choose a matrix that can be cured by a form of radiation other than the type of radiation that is used for writing.

Matrices based on cationic polymerization resins may require photoinitiators based on aromatic diazonium salts, aromatic halonium salts, aromatic sulfonium salts and metallocene compounds. An example of an acceptable matrix includes Nor-Cote CLCDG-1250A or Nor-Cote CDG000 (mixtures of UV curable acrylate monomers and oligomers), which contains a photoinitiator (hydroxy ketone) and organic solvent acrylates (e.g., methyl methacrylate, hexyl

methacrylate, beta-phenoxy ethyl acrylate, and hexamethylene acrylate). Other acceptable matrixes include acrylated polyester oligomers such as CN292, CN293, CN294, SR351 (trimethylolpropane tri acrylate), SR395 (isodecyl acrylate), and SR256 (2(2-ethoxyethoxy) ethyl acrylate) available from Sartomer Co.

5 In some instances, the photochemical and/or photothermal mechanisms that cause the developer precursors to become developers (discussed further hereinbelow) are much slower when the solid matrix is below its glass transition temperature. Without subscribing to a particular theory, the photochemical reactions in solids have an added energy barrier to heat the matrix above its glass
10 transition temperature (T_g). Thus, in some embodiments, it is preferred to provide sufficient photothermal energy in the region of the desired mark 242, 242' to locally heat the matrix above its glass transition temperature T_g . T_g typically depends on the polymer composition of the matrix, and may be selected, if desired, by selecting the polymer that is used for the matrix. In some embodiments, T_g will range from
15 about 120°C to about 300°C.

The layers 230, 232, in some instances, include the same absorber 239, 239' and/or the same contrast agent 240, 240'; and in other instances, each layer 230, 232 includes a different absorber 239, 239' and/or a different contrast agent 240, 240'.

20 The color-forming agent or contrast agent 240, 240' may be any substance that undergoes a detectable optical change in response to a threshold stimulus, which may be applied in the form of light or heat transferred from the absorber 239, 239'. In some embodiments, the contrast agent 240, 240' includes a leuco dye and a developer or a developer precursor, as described in detail below. The developer
25 and the leuco dye produce a detectable optical change when chemically mixed. In other instances, the contrast agent 240, 240' includes a material that, when exposed to energy absorbed by the absorber 239, 239', undergoes changes in absorption coefficient (k), changes in refractive index (n), changes in reflectivity (r), changes in coating dimension (e.g., thickness), or distortion. Generally, the
30 concentration and distribution of the contrast agent 240 in marking layer 230 are

preferably sufficient to produce a detectable mark 242 when activated that is readable through the layer 232.

In a layer 230, 232 in which both the developer and the leuco dye are dissolved, it may be desirable to prevent the components from combining prematurely and generating an optical change across the entire layer 230, 232. This may be accomplished by incorporating one of the components in the layer 230, 232 as a precursor of that component. In these embodiments, the incident light or heat (received from the absorber 239, 239') triggers a chemical change in the precursor, causing it to become the desired component. Once the desired component is formed, both components will be present locally and the contrast-forming reaction occurs. Thus, if energy of the write power and corresponding absorber 239, 239' wavelength is applied to the desired region of layer 230, 232, and the layer 230, 232 is sensitive to the intensity of the applied energy, an optically detectable mark 242, 242' can be produced.

In one embodiment, a developer precursor is in close proximity with the leuco dye in the layer 230, 232. The developer precursor does not become active as a developer until it has absorbed a stimulus which causes it to physically or chemically rearrange. As such, in one instance, the developer precursor also acts as the absorber 239, 239'. After the rearrangement of the developer precursor, it can function as a developer as it comes in contact with the leuco dye. As a result, the matrix may be provided as a homogeneous, single-phase solution at ambient conditions because the use of a precursor for the developer prevents the color-forming/contrast reaction from occurring prior to activation.

Nonetheless, in other embodiments, one or the other of the components may be substantially insoluble in the matrix at ambient conditions. By "substantially insoluble," it is meant that the solubility of that component in the matrix at ambient conditions is so low, that no or very little contrast change occurs due to reaction of the dye and the developer at ambient conditions. Thus, in some embodiments, the developer is dissolved in the matrix with the dye being present as small crystals suspended in the matrix at ambient conditions; while in other embodiments, the

dye is dissolved in the matrix and the developer is present as small crystals suspended in the matrix at ambient conditions. The particle size is preferably less than 400 nm.

Depending on the contrast agent 240, 240' selected and the amount used in
5 the predetermined ratio, the layer 230, 232 may become relatively more or relatively less absorbing at a desired wavelength upon activation. Many commercial and consumer products use a single wavelength of light for both read and write operations, and this has often resulted in a contrast agent 240, 240' that produces a mark 242, 242' that is relatively absorbing (relative to the unmarked
10 regions) for writing as well as for reading at the same wavelength or within the same wavelength range.

When it is desired to make a mark 242, 242', marking energy 110 is directed in a desired manner at imaging medium 100. The form of the energy may vary depending upon the equipment available, ambient conditions, and desired result.
15 Examples of energy that may be used include, but are not limited to, infra-red (IR) radiation, ultra-violet (UV) radiation, x-rays, or visible light. In these embodiments, the recording medium 100 is illuminated with light having the desired predetermined wavelength at the location where it is desired to form a mark 242, 242'. The optical beam is focused on a particular layer 230, 232. It is to be
20 understood that the power required to write to the layer 232 is less than the power required to write to the layer 230 since some power is lost in absorption by the layer 230. Furthermore, the intensity or power of the energy incident upon a particular layer 230, 232 will vary, depending, at least in part, on which layer 230, 232 is to be written to. For example, when writing to the layer 230, it is to be
25 understood that the energy density (energy per unit area) incident upon or absorbed by layer 232 is not sufficient to cause a change. Depending, at least in part, on the focus of the optical beam and the energy density used, the desirable layer 230 or 232 absorbs the energy, causing some physical and/or chemical change therein, resulting in an optically detectable mark 242, 242'. It is to be

understood that the resulting marks 242, 242' can be detected by the previously described optical sensor.

The absorber 239, 239' in the layer 230, 232 absorbs energy density which is effective in producing a mark 242, 242'. For example, the absorber 239 in the
5 first layer 230 will not absorb energy density suitable for writing to the second layer 232, rather it will absorb energy density with sufficient intensity to write the first layer 230. Similarly, the first layer 230 will not receive enough energy density to produce a mark 242 when the beam is focused on the second layer 232. In practice (and as previously mentioned), the energy density used to mark the first
10 layer 230 (i.e., the layer furthest in distance from the optical beam entrance surface) is higher since some energy is lost due to ineffective absorption by the second layer 232.

Once the desirable absorber 239, 239' absorbs the energy, it transfers the energy within the respective layer 230, 232 to the respective contrast agent 240, 240'.
15 240'. The transferred energy triggers a chemical or physical change in the contrast agent 240, 240'. In some instances, the energy causes the developer precursor to convert to the developer and activate the leuco dye. In other instances, the energy causes the contrast agent 240, 240' to experience absorption coefficient changes, refractive index changes, reflectivity changes, dimension (e.g., thickness) changes,
20 or distortion. The activation or change(s) produces an optically detectable mark 242, 242' which may manifest itself in the form of a produced color, a color change and/or a change in the contrast of that particular area of the layer 230, 232. Thus, if energy of a suitable density is applied/focused to a desired region of the layer 230, 232 an optically detectable mark 242, 242' may be produced. Fig. 5 illustrates
25 the transmission stacks for the layers 230, 232, and it is to be understood that the energy density suitable for writing and reading marks 242, 242' is transmissible through the respective stacks.

The absorber dye 239, 239' may be tuned to any desirable wavelength, for example, the absorber dye 239, 239' may have a peak absorption at 405 nm, 650
30 nm, 780 nm, 984 nm or at 1084 nm. It is to be understood that the absorber dye

239, 239' may also be tuned to any desirable absorption band (i.e., the 405 nm band, the 650 nm band, the 780 nm band, the 984 nm band, or the 1084 nm band). As a non-limiting example, the dye may have a peak absorption in the 405 nm band (i.e., ranging from about 375 nm to about 435 nm).

5 Non-limiting examples of suitable absorber dyes 239, 239' with absorption at or near 405 nm (e.g., from about 375 nm to about 435 nm) include curcumin (e.g., curcumin acetate, curcumin benzoate), crocetin, porphyrin and derivatives thereof (e.g., etioporphyrin 1 (CAS 448-71-5), and octaethyl porphyrin (CAS 2683-82-1)), azo dyes (e.g., Mordant Orange (CAS 2243-76-7), Methyl Yellow (CAS 60-11-7), 4-
10 phenylazoaniline (CAS 60-09-3), and Alcian Yellow (CAS 61968-76-1)), C.I. Solvent Yellow 93, C.I. Solvent Yellow 163, ethyl 7-diethylaminocoumarin-3-carboxylate (CAS 28705-46-6), 3,3'-diethylthiacyanine ethylsulfate (CAS 2602-17-7), 3-allyl-5-(3-ethyl-4-methyl-2-thiazolinylidene)rhodanine (CAS 203785-75-5), or the like.

15 Additional examples of suitable absorber dyes 239, 239' include the following: 1) those described in U.S. Patent No. 5,079,135, Japanese Patent 2,910,042 B2, European Patent 0376327B1, and Hong Kong Patent 1007621A1, all of which are assigned to Sony Corporation, Tokyo, and incorporated herein by reference; and 2) those described in U.S. Patent Application Publication No.
20 2002/0015858 and Japanese Patent Application Publication 2002-002112, both of which are assigned to Toyo Ink Mfg. Co. Ltd., Tokyo, and incorporated herein by reference.

 Commercial dyes used in conventional DVD recording, such as IRGAPHOR® Ultragreen MX, IRGAPHOR® LASERVIOLET, and
25 IRGAPHOR® 1699 (all of which are commercially available from Ciba, Tarrytown, NY), may also be effectively used as absorber dyes 239, 239'.

 Still other suitable absorber dyes 239, 239' may be selected from aluminum quinoline complexes, porphyrins, porphins, indocyanine dyes, phenoxazine derivatives, phthalocyanine dyes, polymethyl indolium dyes, polymethine dyes or
30 derivatives thereof (such as a pyrimidinetriene-cyclopentylidene), guaiazulenyl dyes,

croconium dyes, polymethine indolium dyes, metal complex IR dyes, cyanine dyes, squarylium dyes, chalcogeno-pyryloarylidenes dyes, indolizine dyes, pyrylium dyes, quinoid dyes, quinone dyes, azo dyes, and mixtures or derivatives thereof.

Further examples of suitable absorber dyes 239, 239' may also be used, and are known to those skilled in the art and can be found in such references as "Infrared Absorbing Dyes", Matsuoka, Masaru, ed., Plenum Press, New York, 1990 (ISBN 0-306-43478-4) and "Near-Infrared Dyes for High Technology Applications", Daehne, Resch-Genger, Wolfbeis, Kluwer Academic Publishers (ISBN 0-7923-5101-0), both incorporated herein by reference.

The absorber dyes 239, 239' may function as an antenna to absorb electromagnetic radiation of specific wavelengths and ranges. Generally, a radiation antenna which has a predetermined light absorption (dependent, at least in part, on the amount included in the predetermined ratio) at or in the vicinity of the desired development wavelength may be suitable for use in the embodiments disclosed herein. For example, the color forming composition may be optimized within a range for development using infrared radiation of a particular intensity and having a wavelength from about 720 nm to about 900 nm. Common CD-burning lasers have a wavelength of about 780 nm and can be adapted for forming images by selectively developing portions of the image layer. Radiation absorbing compounds/absorber dyes 239, 239' which may be suitable for use in the infrared range include, but are not limited to, polymethyl indoliums, metal complex IR dyes, indocyanine green, polymethine dyes or derivatives thereof (such as pyrimidinetrione-cyclopentylidenes), guaiazulenyl dyes, croconium dyes, cyanine dyes, squarylium dyes, chalcogenopyryloarylidenes dyes, metal thiolate complex dyes, bis(chalcogenopyrylo)polymethine dyes, oxyindolizine dyes, bis(aminoaryl)polymethine dyes, indolizine dyes, pyrylium dyes, quinoid dyes, quinone dyes, phthalocyanine dyes, naphthalocyanine dyes, azo dyes, hexafunctional polyester oligomers, heterocyclic compounds, and combinations thereof. Suitable pyrimidinetrione-cyclopentylidene infrared antennae include, for example, 2,4,6(1H,3H,5H)-pyrimidinetrione 5-[2,5-bis[(1,3-dihydro-1,1,3-dimethyl-

2H-indol-2-ylidene) ethylidene] cyclopentylidene]-1,3-dimethyl- (9CI) (S0322 available from Few Chemicals, Germany).

Several specific polymethyl indolium compounds are available from Aldrich Chemical Company and include 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclopenten-1-yl-ethenyl]-1,3,3-trimethyl-3H-indolium perchlorate; 2-[2-[2-Chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclopenten-1-yl-ethenyl]-1,3,3-trimethyl-3W-indolium chloride; 2-[2-[2-chloro-3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene) ethylidene]-1-cyclohexen-1-yl] ethenyl]-3,3-dimethyl-1-propylindolium iodide; 2-[2-[2-chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene) ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethylindolium iodide; 2-[2-[2-chloro-3-[(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene) ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethylindolium perchlorate; 2-[2-[3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene) ethylidene]-2-(phenylthio)-1-cyclohexen-1-yl] ethenyl]-3,3-dimethyl-1-propylindolium perchlorate; and mixtures thereof.

Alternatively, the absorber dye 239, 239' may be an inorganic compound (e.g., ferric oxide, carbon black, selenium, or the like).

In another embodiment, the absorber dye 239, 239' may be selected for optimization of the color forming composition in a wavelength range from about 600 nm to about 720 nm, such as about 650 nm. Non-limiting examples of suitable absorber dyes 239, 239' for use in this range of wavelengths include indocyanine dyes such as 3H-indolium,2-[5-(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)-1,3-pentadienyl]-3,3-dimethyl-1-propyl-,iodide) (Dye 724 $A_{\max}$ 642 nm), 3H-indolium,1-butyl-2-[5-(1-butyl-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene)-1,3-pentadienyl]-3,3-dimethyl-,perchlorate (Dye 683 $A_{\max}$ 642 nm), and phenoxazine derivatives such as phenoxazin-5-ium,3,7-bis(diethylamino)-,perchlorate (oxazine 1 $A_{\max}$ = 645 nm). Phthalocyanine dyes having an $A_{\max}$ of about the desired development wavelength may also be used, such as, for example, silicon 2,3-naphthalocyanine bis(trihexylsilyloxy) and matrix soluble derivatives of 2,3-naphthalocyanine (both commercially available from Aldrich Chemical); matrix soluble

derivatives of silicon phthalocyanine (as described in Rodgers, A.J. et al., 107 J. Phys. Chem. A 3503-3514, May 8, 2003), and matrix soluble derivatives of benzophthalocyanines (as described in Aoudia, Mohamed, 119 J. Am. Chem. Soc. 6029-6039, July 2, 1997); phthalocyanine compounds, such as those described in
5 U.S. Patent Nos. 6,015,896 and 6,025,486, which are each incorporated herein by reference, and Cirrus 715 (a phthalocyanine dye available from Avecia, Manchester, England having an $A_{\max} = 806$ nm).

As previously mentioned, in some instances, the contrast agent 240, 240' includes a leuco dye and a developer precursor (which receives energy from a
10 separate absorber 239, 239'). In other instances, the contrast agent 240, 240' includes a leuco dye and the absorber 239, 239' functions as the developer precursor.

Specific examples of suitable leuco dyes include fluorans and phthalides, which include but are not limited to the following (which may be used alone or in
15 combination): 1,2-benzo-6-(N-ethyl-N-toluidino)fluoran, 1,2-benzo-6-(N-methyl-N-cyclohexylamino)fluoran, 1,2-benzo-6-dibutylaminofluoran, 1,2-benzo-6-diethylaminofluoran, 2-(.alpha.-phenylethylamino)-6-(N-ethyl-p-toluidino)fluoran, 2-(2,3-dichloroanilino)-3-chloro-6-diethylaminofluoran, 2-(2,4-dimethylanilino)-3-methyl-6-diethylaminofluoran, 2-(di-p-methylbenzilamino)-6-(N-ethyl-p-
20 toluidino)fluoran, 2-(m-trichloromethylanilino)-3-methyl-6-(N-cyclohexyl-N-methylamino)fluoran, 2-(m-trichloromethylanilino)-3-methyl-6-diethylanimofluoran, 2-(m-trifluoromethylaniline)-6-diethylaminofluoran, 2-(m-trifluoromethylanilino)-3-chloro-6-diethylaminofluoran, 2-(m-trifluoromethylanilino)-3-methyl-6-diethylanimofluoran, 2-(N-ethyl-p-toluidino)-3-methyl-6-(N-ethylanilino)fluoran, 2-
25 (N-ethyl-p-toluidino)-3-methyl-6-(N-propyl-p-toluidino) fluoran, 2-(o-chloroanilino)-3-chloro-6-diethylaminofluoran, 2-(o-chloroanilino)-6-dibutylaminofluoran, 2-(o-chloroanilino)-6-diethylaminofluoran, 2-(p-acetylanilino)-6-(N-n-amyl-N-n-butylamino)fluoran, 2,3-dimethyl-6-dimethylaminofluoran, 2-amino-6-(N-ethyl-2,4-dimethylanilino)fluoran, 2-amino-6-(N-ethylanilino)fluoran, 2-amino-6-(N-ethyl-p-chloroanilino)fluoran, 2-amino-6-(N-ethyl-p-ethylanilino)fluoran, 2-amino-6-(N-ethyl-

p-toluidino)fluoran, 2-amino-6-(N-methyl-2,4-dimethylanilino)fluoran, 2-amino-6-(N-methylanilino)fluoran, 2-amino-6-(N-methyl-p-chloroanilino)fluoran, 2-amino-6-(N-methyl-p-ethylanilino)fluoran, 2-amino-6-(N-methyl-p-toluidino)fluoran, 2-amino-6-(N-propyl-2,4-dimethylanilino)fluoran, 2-amino-6-(N-propylanilino)fluoran, 2-amino-6-(N-propyl-p-chloroanilino)fluoran, 2-amino-6-(N-propyl-p-ethylanilino)fluoran, 2-amino-6-(N-propyl-p-toluidino)fluoran, 2-anilino-3-chloro-6-diethylaminofluran, 2-anilino-3-methyl-6-(N-cyclohexyl-N-methylamino)fluoran, 2-anilino-3-methyl-6-(N-ethyl--N-isoamylamino)fluoran, 2-anilino-3-methyl-6-(N-ethyl-N-p-benzyl)aminofluoran, 2-anilino-3-methyl-6-(N-ethyl-N-propylamino)fluoran, 2-anilino-3-methyl-6-(N-iso-amyl-N-ethylamino)fluoran, 2-anilino-3-methyl-6-(N-isobutyl-methyl amino)fluoran, 2-anilino-3-methyl-6-(N-isopropyl-methyl amino)fluoran, 2-anilino-3-methyl-6-(N-methyl-p-toluidino-)fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-ethylamino)fluoran, 2-anilino-3-methyl-6-(N-n-amyl-N-methylamino)fluoran, 2-anilino-3-methyl-6-(N-n-propyl-N-isopropylamino)fluoran, 2-anilino-3-methyl-6-(N-n-propyl-N-methylamino)fluoran, 2-anilino-3-methyl-6-(N-sec-butyl-N-methylamino)fluoran, 2-anilino-3-methyl-6-diethylaminofluoran, 2-anilino-3-methyl-6-di-n-butylaminofluoran, 2-anilino-6-(N-n-hexyl-N-ethylamino)fluoran, 2-benzilamino-6-(N-ethyl-2,4-dimethylanilino)fluoran, 2-benzilamino-6-(N-ethyl-p-toluidino)fluoran, 2-benzilamino-6-(N-methyl-2,4-dimethylanilino)fluoran, 2-benzilamino-6-(N-methyl-p-toluidino)fluoran, 2-bromo-6-diethylaminofluoran, 2-chloro-3-methyl-6-diethylaminofluran, 2-chloro-6-(N-ethyl-N-isoamylamino)fluoran, 2-chloro-6-diethylaminofluoran, 2-chloro-6-dipropylaminofluoran, 2-diethylamino-6-(N-ethyl-p-toluidino)fluoran, 2-diethylamino-6-(N-methyl-p-toluidino)fluoran, 2-dimethylamino-6-(N-ethylanilino)fluoran, 2-dimethylamino-6-(N-methylanilino)fluoran, 2-dipropylamino-6-(N-ethylanilino)fluoran, 2-dipropylamino-6-(N-methylanilino)fluoran, 2-ethylamino-6-(N-ethyl-2,4-dimethylanilino)fluoran, 2-ethylamino-6-(N-methyl-p-toluidino)fluoran, 2-methylamino-6-(N-ethylanilino)fluoran, 2-methylamino-6-(N-methyl-2,4-dimethylanilino)fluoran, 2-methylamino-6-(N-methylanilino)fluoran, 2-methylamino-6-(N-propylanilino)fluoran, 3-(1-ethyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide,

3-(1-ethyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-7-azaphthalide,
3-(1-ethyl-2-methylindole-3-yl)-3-(2-methyl-4-diethylaminophenyl)-4-azaphthalide,
3-(1-ethyl-2-methylindole-3-yl)-3-(2-methyl-4-diethylaminophenyl)-7-azaphthalide,
3-(1-ethyl-2-methylindole-3-yl)-3-(4-diethylaminophenyl)-4-azaphthalide, 3-(1-ethyl-
5 2-methylindole-3-yl)-3-(4-N-n-amy-N-methylaminophenyl)-4-azaphthalide, 3-(1-
methyl-2-methylindole-3-yl)-3-(2-hexyloxy-4-diethylaminophenyl)-4-azaphthalide, 3-
(1-ethyl-2-methylindole-3-yl)-3-(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide, 3-
(N-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-N-
isoamylamino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-
10 phenylaminofluoran, 3,3-bis(2-ethoxy-4-diethylaminophenyl)-4-azaphthalide, 3,3-
bis(2-ethoxy-4-diethylaminophenyl)-7-azaphthalide, 3,6-dibutoxyfluoran, 3,6-
diethoxyfluoran, 3,6-dimethoxyfluoran, 3-bromo-6-cyclohexylaminofluoran, 3-
chloro-6-cyclohexylaminofluoran, 3-dibutylamino-7-(o-chloro-phenylamino)fluoran,
3-diethylamino-5-methyl-7-dibenzylaminofluoran, 3-diethylamino-6-(m-
15 trifluoromethylanilino)fluoran, 3-diethylamino-6,7-dimethylfluoran, 3-diethylamino-6-
methyl-7-xylidinofluoran, 3-diethylamino-7-(2-carbomethoxy-phenylamino)fluoran,
3-diethylamino-7-(N-acetyl-N-methylamino)fluoran, 3-diethylamino-7-(N-
chloroethyl-N-methylamino)fluoran, 3-diethylamino-7-(N-methyl-N-
benzylamino)fluoran, 3-diethylamino-7-(o-chlorophenylamino)fluoran, 3-
20 diethylamino-7-chlorofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-
diethylamino-7-diethylaminofluoran, 3-diethylamino-7-N-methylaminofluoran, 3-
dimethylamino-6-methoxyfluoran, 3-dimethylamino-7-methoxyfluoran, 3-methyl-6-
(N-ethyl-p-toluidino)fluoran, 3-piperidino-6-methyl-7-phenylaminofluoran, 3-
pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, and 3-pyrrolidino-6-methyl-7-
25 phenylaminofluoran.

Additional dyes that may be alloyed in embodiments disclosed herein include, but are not limited to leuco dyes such as fluoran leuco dyes and phthalide contrast formers as are described in "The Chemistry and Applications of Leuco Dyes," Muthyala, Ramiah, ed., Plenum Press (1997) (ISBN 0-306-45459-9).

30 Embodiments of the markable coating 230 may include almost any known leuco

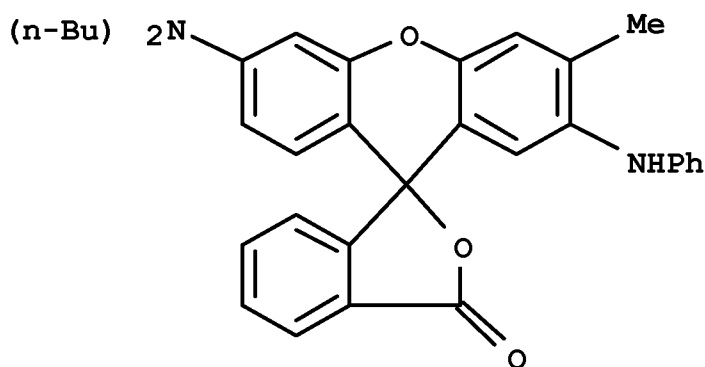
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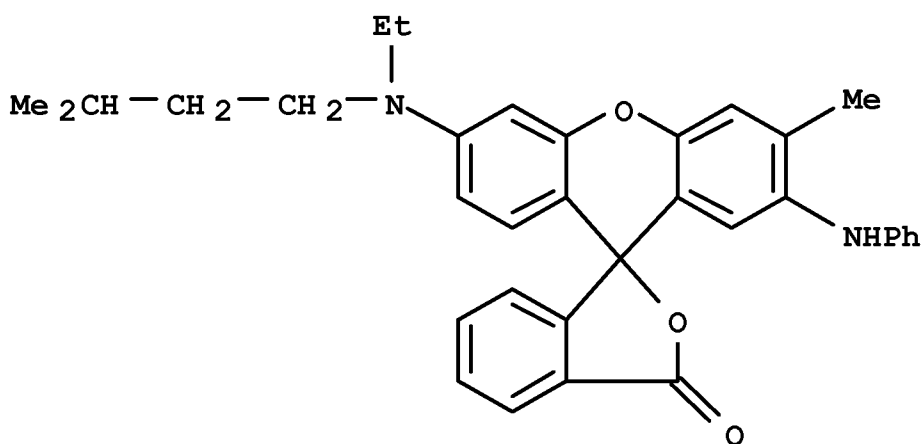
dye, including, but not limited to, amino-triarylmethanes, aminoxanthenes, aminothioxanthenes, amino-9, 10-dihydro-acridines, aminophenoxazines, aminophenothiazines, aminodihydro-phenazines, aminodiphenylmethanes, aminohydrocinnamic acids (cyanoethanes, leuco methines) and corresponding
 5 esters, 2(p-hydroxyphenyl)-4, 5-diphenylimidazoles, indanones, leuco indamines, hydrozines, leuco indigoid dyes, amino-2, 3-dihydroanthraquinones, tetrahalo-p, p'-biphenols, 2(p-hydroxyphenyl)-4, 5-diphenylimidazoles, phenethylanilines, and mixtures thereof.

Particularly suitable leuco dyes include:

10 2'-anilino-3'-methyl-6'-(dibutylamino)-fluoran:

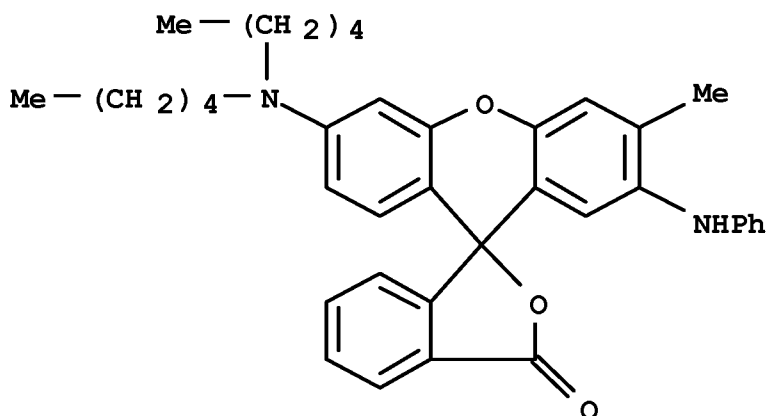


20 2-anilino-3-methyl-6-(N-ethyl-N-isoamylamino)fluoran:



, and

2-anilino-3-methyl-6-(di-n-amylamino)fluoran:



All three of the previously listed dyes are commercially available from Nagase Co of Japan. Additional examples of suitable dyes include: Pink DCF (CAS 29199-09-5); Orange-DCF (CAS 21934-68-9); Red-DCF (CAS 26628-47-7); Vermilion-DCF (CAS 117342-26-4); bis(dimethyl)aminobenzoyl phenothiazine (CAS 1249-97-4); Green-DCF (CAS 34372-72-0); chloroanilino dibutylaminofluoran (CAS 82137-81-3); NC-Yellow-3 (CAS 36886-76-7); Copikem37 (CAS 144190-25-0); Copikem3 (CAS 22091-92-5), available from Hodogaya, Japan or Noveon, Cincinnati, USA.

Still other non-limiting examples of suitable fluoran-based leuco dyes include: 3-diethylamino-6-methyl-7-anilino-fluoran 3-(N-ethyl-p-toluidino)-6-methyl-7-anilino-fluoran, 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-6-methyl-7-(o,p-dimethylanilino)fluorane, 3-pyrrolidino-6-methyl-7-anilino-fluoran, 3-piperidino-6-methyl-7-anilino-fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-7-(m-trifluoromethylanilino)fluoran, 3-dibutylamino-6-methyl-7-anilino-fluoran, 3-diethylamino-6-chloro-7-anilino-fluoran, 3-dibutylamino-7-(o-chloroanilino)fluoran, 3-diethylamino-7-(o-chloroanilino)fluoran 3-di-n-pentylamino-6-methyl-7-anilino-fluoran, 3-di-n-butylamino-6-methyl-7-anilino-fluoran, 3-(n-ethyl-n-isopentylamino)-6-methyl-7-anilino-fluoran, 3-pyrrolidino-6-methyl-7-anilino-fluoran, 1(3H)-isobenzofluranone,

4,5,6,7-tetrachloro-3, 3-bis [2-[4-(dimethylamino)phenyl]-2-(4-methoxyphenyl)ethenyl] fluoran, and mixtures thereof. Aminotriarylmethane leuco dyes may also be used in embodiments of the present invention such as tris(N,N-dimethylaminophenyl) methane (LCV); tris(N,N-diethylaminophenyl) methane (LECV); tris(N,N-di-n-propylaminophenyl) methane (LPCV); tris(N,N-di-n-butylaminophenyl) methane (LBCV); bis(4-diethylaminophenyl)-(4-diethylamino-2-methyl-phenyl) methane (LV-1); bis(4-diethylamino-2-methylphenyl)-(4-diethylamino-phenyl) methane (LV-2); tris(4-diethylamino-2-methylphenyl) methane (LV-3); bis(4-diethylamino-2-methylphenyl) (3,4-dimethoxyphenyl) methane (LB-8); aminotriarylmethane leuco dyes having different alkyl substituents bonded to the amino moieties wherein each alkyl group is independently selected from C₁-C₄ alkyl; and aminotriarylmethane leuco dyes with any of the preceding named structures that are further substituted with one or more alkyl groups on the aryl rings wherein the latter alkyl groups are independently selected from C₁-C₃ alkyl.

Any suitable developer may be used with these leuco dyes. According to certain embodiments, the desired developer is provided in the form of a precursor that can be photochemically or photothermally modified to become the desired developer. As previously mentioned, by providing the developer in precursor form, the need to physically separate the developer from the dye is eliminated. For example, rather than providing one of the color-forming components as particles that are suspended in the matrix, both the dye and the developer precursor can be dissolved in the matrix.

Developer precursors suitable for use in the embodiments disclosed herein, without limitation, include some of the examples previously set forth for the absorber 239, 239', such as curcumin. It is to be understood that the following absorbers 239, 239' generally do not exhibit a developer function (and as such, are included with an additional developer) include crocetin, porphyrin and derivatives thereof (e.g., etioporphyrin 1 (CAS 448-71-5), and octaethyl porphyrin (CAS 2683-82-1)), azo dyes (e.g., Mordant Orange (CAS 2243-76-7), Methyl Yellow (CAS 60-11-7), 4-phenylazoaniline (CAS 60-09-3), and Alcian Yellow (CAS 61968-76-1)),

C.I. Solvent Yellow 93, C.I. Solvent Yellow 163, ethyl 7-diethylaminocoumarin-3-carboxylate (CAS 28705-46-6), 3,3'-diethylthiacyanine ethylsulfate (CAS 2602-17-7), 3-allyl-5-(3-ethyl-4-methyl-2-thiazolinyldene)rhodanine (CAS 203785-75-5), or the like.

5 Other suitable developer precursors involving photochemical reactions are phenyl esters that undergo a molecular rearrangement so as to become phenolic compounds capable of developing (activating) the leuco dye. Such rearrangements are sometimes referred to as Fries rearrangements. It is to be understood that Fries rearrangements may be thermally driven. In some instances,
10 esters may undergo photo-initiated Fries rearrangements (sometimes referred to as Photo Fries rearrangements). Both types of rearrangement (thermal- and photo-driven) are within the scope of the disclosed embodiments, and that the stimulus for such rearrangements may be light, heat, or a combination thereof. These developer precursors may function as the absorber 239, 239', or may be
15 used as a component of the contrast agent 240, 240' that receives energy from another absorber 239, 239'.

In certain embodiments, suitable developer precursors include compounds having the formula:



20 where R is an aryl group and R' is an alkyl or aryl group. Exemplary compounds include, but are not limited to, di-O-acetylated and di-O-benzoylated curcuminoids. Alternatively, any aryl ester that absorbs or has a peak absorption wavelength ranging from about 380 nm to about 420 nm, and more particularly from about 400 nm to about 410 nm may be a developer precursor suitable for use herein. These
25 developer precursors are suitable absorbers 239, 239' for the leuco dyes.

Other suitable ester precursors of developers include bisphenol-A, bisphenol-S, hydroxy benzyl benzoates, TG-SA (phenol, 4,4'-sulfonylbis[2-(2-propenyl)]) and poly-phenols.

An example of a contrast agent 240, 240' that experiences absorption
30 coefficient changes, refractive index changes, reflectivity changes, dimension (e.g.,

thickness) changes, and/or distortion includes silicon naphthalocyanine (SiNc) (CAS 92396-88-8) available from Aldrich (which, when including trihexyloxy substituents, has sufficient solubility in UV lacquer or other solvents of the markable coatings 230). Other examples of such contrast agents 240, 240' include

5 PRO-JET™ 800NP, PRO-JET™ 830NP, PRO-JET™ 900NP, all of which are commercially available from Fujifilm, UK, as imaging colorants for inkjet applications.

Modulation and reflectivity of the layers 230, 232 are generally defined in terms of the photo current from light received by the sensor. The modulation and

10 reflectivity produced from a particular composition/layer 230, 232 is dependent on many factors, including, but not limited to groove width, depth, layer thickness, absorption coefficients of absorber (239, 239') and contrast agent (240, 240'), refractive index, and layer structure. The desirable modulation and reflectivity for the recording medium 100 disclosed herein is shown in Table 1.

15

Table 1

Parameter	Dual Layer Recording Medium
Reflectivity of virgin grooves R_{g-v}	3.5 to 9%
Reflectivity of Recorded grooves R_{8H}	3 to 9%
Reflectivity at each location on disc	$0.76 \cdot R_{g-v} < R_{8H} < 1.26 \cdot R_{g-v}$
Modulation measured as ratio of the Photo Currents	$I_{8top}/I_{8pp} > 0.39$ AND $I_{3top}/I_{3pp} > 0.24$
Ratio of modulation currents from top (Lt) and bottom (Lb) layer in a two layer system	$(-0.24 \leq I_{8HLt} - I_{8HLb}) / (I_{8HLt} - I_{8HLb}) \leq 0.25$

Fig. 6 illustrates a non-limiting example of HF signals received from the elements of a photo detector when reading an optical disc 100. The respective

20 numbers show the signal from a mark 242 of a particular length. For example, I8

denotes an 8T mark (where "T" is mark length (proportional to time)), and I3 denotes a 3T mark, and pp denotes 'peak to peak' amplitude. The following compositions are examples of compositions that produce signals in the desirable ranges outlined in Table 1.

5

Example 1

Layer	Absorber 239, 239'	Contrast Agent 240, 240'	Total Concentration, Ratio of 239, 239':240, 240'
Layer 232	S0512	JM42B	140 mg/mL , 1:0.4
Layer 230	S0512	JM42B	240mg/mL 1:1

Example 2

Layer	Absorber 239, 239'	Contrast Agent 240, 240'	Total Concentration, Ratio of 239, 239':240, 240'
Layer 232	C.I. Solvent Yellow 93	CIBA UltraGreen	50mg/mL, 1:5
Layer 230	C.I. Solvent Yellow 93	CIBA UltraGreen	50mg/mL 1:4

It is to be understood that additional (e.g., three or more) layers (not shown) may also be included in the markable coating. Such layers are formulated with an absorber 239, 239' and a contrast agent 240, 240' and are suitable for writing and reading. The position of such additional layers within the medium 100 will assist in determining the predetermined ratio of each such layer. For example, it is desirable that the additional layers exhibit respective sensitivity and contrast that enables each of the other layers 230, 232 to be written to and read.

Radiation sources (e.g., a laser or LED) having blue, indigo, red and far-red wavelengths ranging from about 300 nm to about 980 nm may be used to develop the layers 230, 232 described herein. Therefore, recording/imaging media 100 may be selected for use in devices that emit wavelengths within this range. For example, if the light source 150 emits light having a wavelength of about 405 nm, the absorber dye 239, 239' may be selected to absorb energy at or near that

wavelength/wavelength band and emitted at a predetermined intensity. In other embodiments, light sources 150 of other wavelengths/wavelength bands, including but not limited to 650 nm, 780 nm, 984 nm or 1084 nm may be used. In either case, the absorber dye 239, 239' may be tuned to the selected

5 wavelength/wavelength band so as to enhance localized energy absorption.

By way of example, if blue-violet light (radiation) is to be used as the read radiation, the marks 242, 242' formed in the marking layer 230, 242 are preferably a contrasting color, namely yellow to orange, indicating absorption of blue radiation. Furthermore, the marks 242 formed in the marking layer 230 exhibit a
10 darker contrast than the marks 242' in the marking layer 232. In certain embodiments, therefore, the layer 230, 232 contains a contrast agent 240, 240' that, when activated, changes from being relatively non-absorbing at blue-violet wavelengths to being relatively absorbing at those wavelengths.

The imaging compositions formed in the manner described herein can be
15 applied to the surface of a disc, such as a CD, DVD, HD-DVD, BLU-RAY disc, or the like. Further, discs may be used in systems disclosed herein that include optical recording and/or reading capabilities. Such systems typically include a laser emitting light (e.g., light source 150) having a predetermined wavelength and power.

20 As previously discussed hereinabove, when it is desired to record, the imaging medium 100 is positioned such that light emitted by laser 150 is sufficient to record to one of the layers 230 or 232 at any given instant. The laser 150 is operated such that the light incident on the respective layer 230, 232 transfers sufficient energy density to the surface to cause a mark 242, 242'. Both the laser
25 150 and the position of the imaging medium 100 are controlled by the processor 166, such that light is emitted by the laser 150 in pulses that form a pattern of marks 242, 242' on the surface of the desirable layer 230, 232 of the imaging medium 100.

When it is desired to read a pattern of marks 242, 242' on the surface of a
30 layer 230, 232, the imaging medium 100 is again positioned such that light emitted

by laser 150 is incident on the medium 100. By varying the optics offset and the specified sum signal, the system may be configured to focus on a particular plane of the markable coating, thereby reading a particular layer 230, 232. The laser 150 is operated such that the light focuses on a particular plane of the markable
5 coating, and is incident at the desirable surface so as to not transfer sufficient energy to cause a mark 242, 242'. Instead, the incident light is reflected from the marked surface to a greater or lesser degree, depending on the absence or presence of a mark 242, 242'. As the imaging medium 100 moves, changes in reflectance are recorded by optical pickup 157 which generates a signal 165
10 corresponding to the marked surface. Both the laser 150 and the position of the imaging medium 100 are controlled by the processor 166 during the reading process.

It is be understood that the read/write system 170 described herein is merely exemplary and includes components that are understood in the art. Various
15 modifications can be made, including the use of multiple lasers, processors, and/or pickups and the use of light having different wavelengths. The read components may be separated from the write components, or may be combined in a single device.

While several embodiments have been described in detail, it will be
20 apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting.

What is claimed is:

1. An optical data recording medium (100), comprising:
a substrate (220);
a first layer (230) of a markable coating established on the substrate (220)
5 and including a first predetermined ratio of a first absorber dye (239) and a first
contrast-forming agent (240); and
a second layer (232) of the markable coating established on the first layer
(220) of the markable coating and including a second predetermined ratio of a
second absorber dye (239') and a second contrast-forming agent (240') that is
10 different from the first predetermined ratio of the first absorber dye (239) and first
contrast-forming agent (240).
2. The optical data recording medium (100) as defined in claim 1 wherein
the first and second absorber dyes (239, 239') are independently selected from a
15 dye having a peak absorption at a 405 nm band, a dye having a peak absorption at
a 650 nm band, a dye having a peak absorption at a 780 nm band, a dye having a
peak absorption at a 984 nm band, or a dye having a peak absorption at a 1084
nm band.
- 20 3. The optical data recording medium (100) as defined in any of claims 1 or
2 wherein the first predetermined ratio is selected to obtain an optical density
difference of the first layer (230) ranging from about 0.15 to about 0.20, and
wherein the second predetermined ratio is selected to obtain an optical density
difference of the second layer (232) ranging from about 0.20 to about 0.40.
- 25 4. The optical data recording medium (100) as defined in any of claims 1
through 3 wherein the first and second predetermined ratios are selected such that
reflectivity of virgin grooves (R_{g-v}) ranges from about 3.5% to about 9%; reflectivity
of recorded grooves (R_{8H}) ranges from about 3% to about 9%; $0.76 \cdot R_{g-}$

$\sqrt{R_{8H}} < 1.26 \cdot R_{g-v}$; $I_{8top}/I_{8pp} > 0.39$ and $I_{3top}/I_{3pp} > 0.24$; and $(-0.24 < I_{8HLt} - I_{8HLb}) / (I_{8HLt} - I_{8HLb}) < 0.25$).

5 5. The optical data recording medium (100 as defined in any of claims 1 through 4 wherein the first layer (230) is configured to produce a first optically detectable mark (242), wherein the second layer (232) is configured to produce a second optically detectable mark (242'), and wherein the first and second optically detectable marks (242, 242') exhibit a different contrast.

10 6. The optical data recording medium (100) as defined in claim 6 wherein the first optically detectable mark (242) is readable through the second layer (232).

15 7. The optical data recording medium (100) as defined in claim 1 wherein the first and second absorber dyes (239, 239') exhibit different intensities of absorbance at a predetermined wavelength.

8. A system for at least one of recording or transmitting optical data or visual images, comprising:

an optical data or visual image recording medium (100) including:

20 a substrate (220);
 a first layer (230) of a markable coating established on the substrate (220) and including a first predetermined ratio of a first absorber dye (239) and a first contrast-forming agent (240); and
 a second layer (232) of the markable coating established on the first
 25 layer (230) of the markable coating and including a second predetermined ratio of a second absorber dye (239') and a second contrast-forming agent (240') that is different from the first predetermined ratio of the first absorber dye (239) and first contrast-forming agent (240); and

a light source (150) positioned so as to illuminate the recording medium (100) in a predetermined manner to i) cause the first absorber dye (239) to capture light energy from the light source (150) and transfer such light energy to the first contrast-forming agent (240) to form an optically detectable mark (242) on the first layer (230), ii) cause the second absorber dye (239') to capture light energy from the light source (150) and transfer such light energy to the second contrast-forming agent (240') to form an optically detectable mark (242') on the second layer (232), or iii) cause at least one optically detectable mark (242, 242') previously formed on the first layer (230) or the second layer (232) to produce at least one readable pattern.

9. The system as defined in claim 8 wherein the first and second absorber dyes (239, 239') are independently selected from a dye having a peak absorption at a 405 nm band, a dye having a peak absorption at a 650 nm band, a dye having a peak absorption at a 780 nm band, a dye having a peak absorption at a 984 nm band, or a dye having a peak absorption at a 1084 nm band.

10. The system as defined in any of claims 8 or 9 wherein the first and second predetermined ratios are selected such that reflectivity of virgin grooves (R_{g-v}) ranges from about 3.5% to about 9%; reflectivity of recorded grooves (R_{8H}) ranges from about 3% to about 9%; $0.76 \cdot R_{g-v} < R_{8H} < 1.26 \cdot R_{g-v}$; $I_{8top}/I_{8pp} > 0.39$ and $I_{3top}/I_{3pp} > 0.24$; and $(-0.24 < I_{8HLL} - I_{8HLLb}) / (I_{8HLL} - I_{8HLLb}) < 0.25$.

11. The system as defined in any of claims 8 through 10 wherein the optically detectable mark (242) on the first layer (230) exhibits a different contrast than the optically detectable mark (242') on the second layer (232).

12. The system as defined in any of claims 8 through 11 wherein the first and second absorber dyes (239, 239') exhibit different intensities of absorbance at a predetermined wavelength.

5 13. The system as defined in any of claims 8 through 12 wherein for optically transmitting data and visual images, the system further comprises:

 a sensor (157) positioned so as to focus a laser on a plane of the first layer (230) or a plane of the second layer (232) having the at least one previously formed optically detectable mark (242, 242') thereon, and to detect the at least one
10 readable pattern, the sensor (157) reading the at least one readable pattern as the medium (100) moves in relation to the sensor (157);

 a processor (166) to which the sensor (157) sends at least one signal based on the at least one readable pattern detected by the sensor (157);

 an analyzer (168) to which the processor (166) sends the at least one
15 signal, the analyzer (168) configured to analyze the at least one signal and generate data therefrom; and

 a computer data base (114) configured to receive and store the data from the analyzer (168), wherein the data is accessible via the computer data base (114).

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14. A method for at least one of i) optically recording data or visual images, or ii) reading optically recorded data or visual images, the method comprising:

 providing an optical data or visual image recording medium (100), including:

 a substrate (220);

25 a first layer (230) of a markable coating established on the substrate (220) and including a first predetermined ratio of a first absorber dye (239) and a first contrast-forming agent (240); and

 a second layer (232) of the markable coating established on the first layer (230) of the markable coating and including a second predetermined
30 ratio of a second absorber dye (239') and a second contrast-forming agent

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(240') that is different from the first predetermined ratio of the first absorber dye (239) and first contrast-forming agent (240); and
beaming light from a light source (150) to i) cause the first absorber dye (239) to capture light energy from the light source (150) and transfer such light
5 energy to the first contrast-forming agent (240) to form an optically detectable mark (242) on the first layer (230), ii) cause the second absorber dye (239') to capture light energy from the light source (150) and transfer such light energy to the second contrast-forming agent (240') to form an optically detectable mark (242') on the second layer (232), or iii) cause at least one optically detectable mark (242, 242')
10 previously formed on the first layer (230) or the second layer (232) to produce at least one readable pattern.

15. The method as defined in claim 14 wherein the at least one previously formed optically detectable mark (242, 242') produces the at least one readable
15 pattern, and wherein the method further comprises:
focusing a laser of a sensor (157) on a plane of the first layer (230) or a plane of the second layer (232) having the at least one previously formed optically detectable mark (242, 242') thereon;
detecting the at least one readable pattern via the sensor (157) reading the
20 at least one readable pattern as the medium (100) moves in relation to the sensor (157); and
sending from the sensor (157) to a processor (166) at least one signal based on the at least one readable pattern detected by the sensor (157).

25 16. The method as defined in any of claims 14 or 15 wherein the first and second absorber dyes (239, 239') exhibit different intensities of absorbance at the predetermined wavelength.

17. The method as defined in claim 16 wherein the predetermined wavelength is selected from a 405 nm band, a 650 nm band, a 780 nm band, a 984 nm band, or a 1084 nm band.

5 18. A method of making an optical data recording medium (100), the method comprising:

 establishing first and second layers (230, 232) of a markable coating on a substrate (220), the first layer (230) including a first predetermined ratio of a first absorber dye (239) and a first contrast-forming agent (240), and the second layer
10 (232) including a second predetermined ratio of a second absorber dye (239') and a second contrast-forming agent (240'); and

 tuning at least one of the first predetermined ratio or the second predetermined ratio such that i) the first and second contrast agents (240, 240') exhibit different intensities of absorbance at a predetermined wavelength, and ii) an
15 optically detectable mark (242) formed in the first layer (230) exhibits a different contrast than an optically detectable mark (242') formed in the second layer (232).

 19. The method as defined in claim 18 wherein the first predetermined ratio is selected to obtain an optical density difference of the first layer (230) ranging
20 from about 0.15 to about 0.20, and wherein the second predetermined ratio is selected to obtain an optical density difference of the second layer (232) ranging from about 0.20 to about 0.40.

 20. An apparatus for at least one of recording or transmitting optical data or
25 visual images, comprising:

 an optical data or visual image recording medium (100), including:

 a substrate (220);

 a first layer (230) of a markable coating established on the substrate (220) and including a first predetermined ratio of a first absorber dye (239)

30 and a first contrast-forming agent (240); and

a second layer (232) of the markable coating established on the first layer (230) of the markable coating and including a second predetermined ratio of a second absorber dye (239') and a second contrast-forming agent (240') that is different from the first predetermined ratio of the first absorber dye (239) and first contrast-forming agent (240); and

5 a recording or transmitting device including a light source (150) positioned to transmit light beams to at least one of i) cause the first absorber dye (238) to capture light energy from the light source (150) and transfer such light energy to the first contrast-forming agent (240) to form an optically detectable mark (242) on the first layer (230), ii) cause the second absorber dye (239') to capture light

10 energy from the light source (150) and transfer such light energy to the second contrast-forming agent (240') to form an optically detectable mark (242') on the second layer (232), or iii) cause at least one optically detectable mark (242, 242') previously formed on the first layer (230) or the second layer (232) to produce at

15 least one readable pattern.

21. The apparatus as defined in claim 20 wherein the first predetermined ratio is selected to obtain an optical density difference of the first layer (230) ranging from about 0.15 to about 0.20, and wherein the second predetermined ratio

20 is selected to obtain an optical density difference of the second layer (232) ranging from about 0.20 to about 0.40.

22. The apparatus as defined in any of claims 20 or 21 wherein the first and second predetermined ratios are selected such that reflectivity of virgin grooves

25 (R_{g-v}) ranges from about 3.5% to about 9%; reflectivity of recorded grooves (R_{8H}) ranges from about 3% to about 9%; $0.76 \cdot R_{g-v} < R_{8H} < 1.26 \cdot R_{g-v}$; $I_{8top}/I_{8pp} > 0.39$ and $I_{3top}/I_{3pp} > 0.24$; and $(-0.24 < I_{8HLt} - I_{8HLb}) / (I_{8HLt} - I_{8HLb}) < 0.25$.

23. The apparatus as defined in any of claims 20 through 23 wherein the optically detectable mark (242) formed on the first layer (230) exhibits a different contrast than the optically detectable mark (242') formed on the second layer (232).

5 24. The apparatus as defined in any of claims 20 through 23 wherein the first and second absorber dyes (239, 239') exhibit different intensities of absorbance at a predetermined wavelength.

10 25. The apparatus as defined in any of claims 20 through 24 wherein for optically transmitting data or visual images, the apparatus further comprises:
 a sensor (157) positioned so as to focus a laser on a plane of the first layer (230) or a plane of the second layer (232) having the at least one previously formed optically detectable mark (242, 242') thereon, and to detect the at least one readable pattern as the recording medium (100) moves in relation to the sensor
15 (157); and
 a processor (166) to which the sensor (157) sends at least one signal based on the at least one readable pattern detected by the sensor (157).

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INITIAL ABSORBANCE OF MARKED AND UNMARKED COATINGS

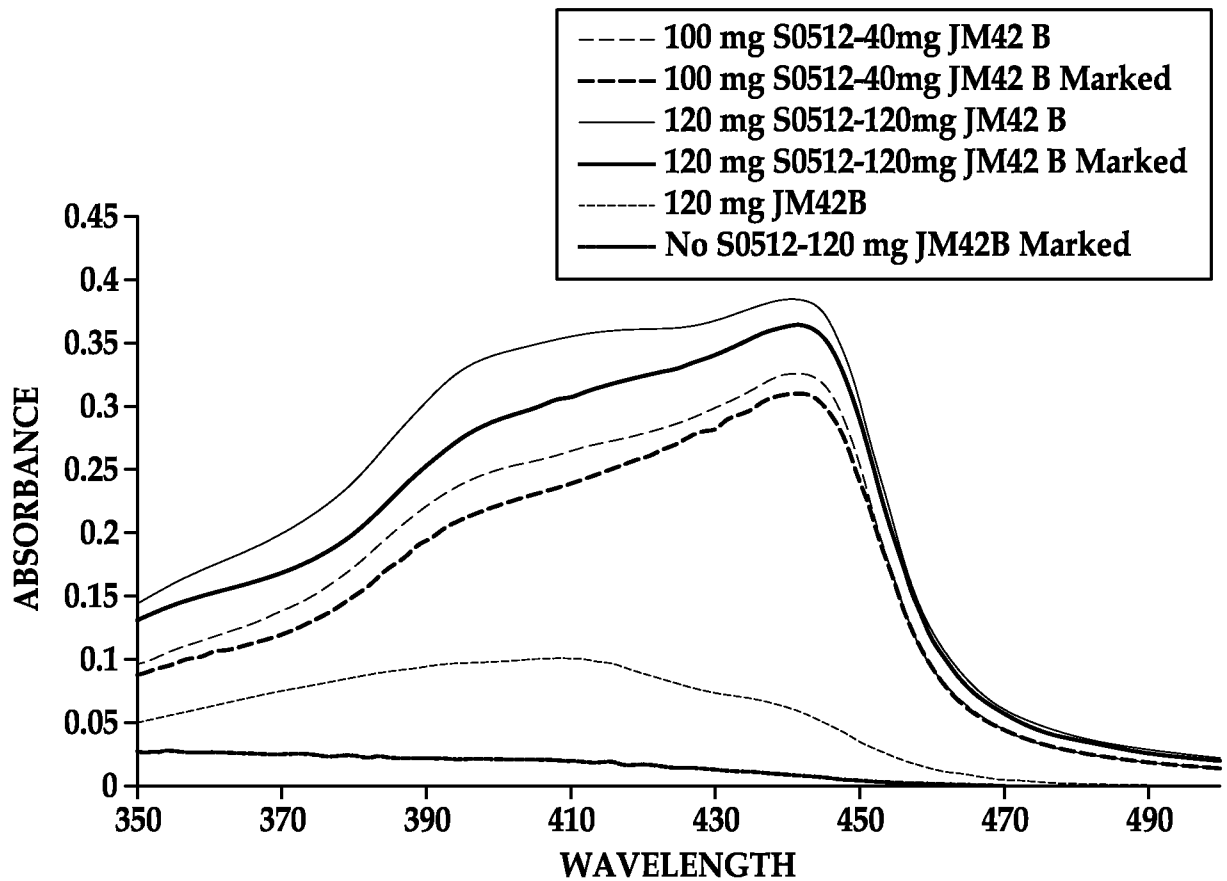


FIG. 1A

CONTRAST DIFFERENCE BETWEEN MARKED AND UNMARKED COATINGS

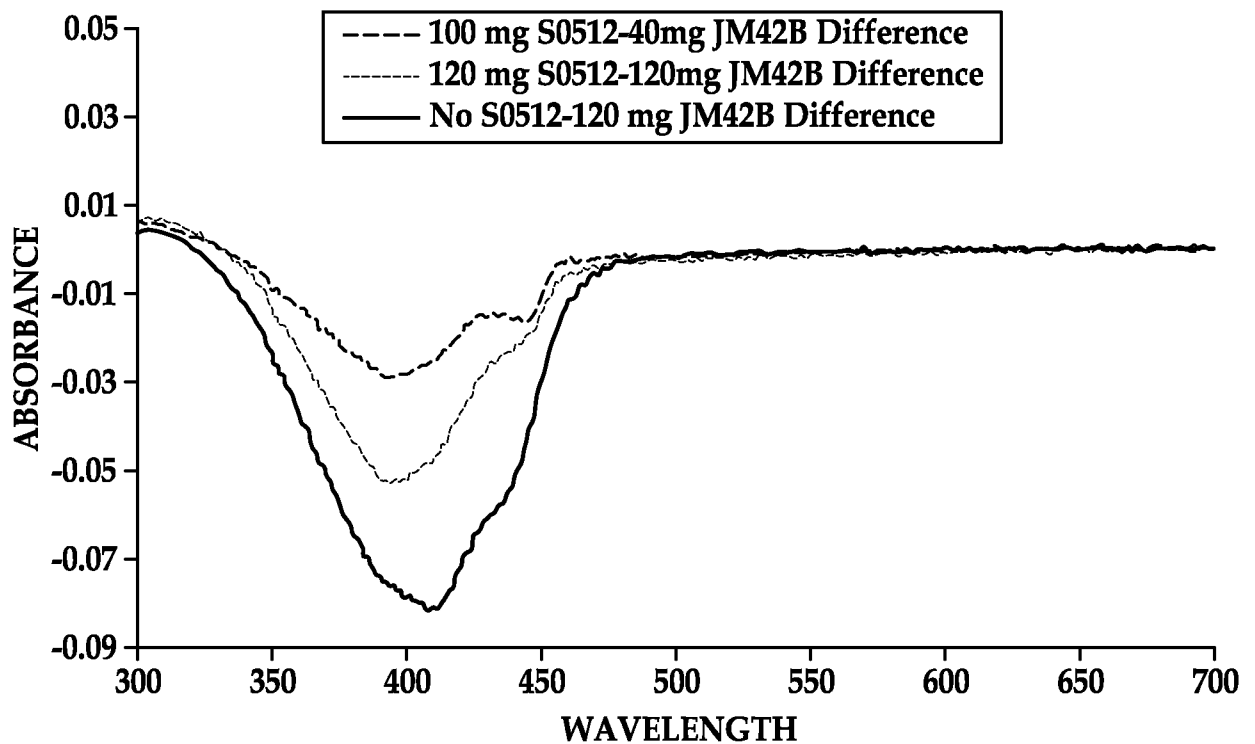


FIG. 1B

**ESTABLISHING FIRST AND SECOND LAYERS OF A MARKABLE COATING
ON A SUBSTRATE, THE FIRST LAYER INCLUDING A FIRST PREDETERMINED
RATIO OF A FIRST ABSORBER DYE AND A FIRST CONTRAST-FORMING
AGENT, AND THE SECOND LAYER INCLUDING A SECOND PREDETERMINED
RATIO OF A SECOND ABSORBER DYE AND A SECOND CONTRAST-FORMING
AGENT**

TUNING AT LEAST ONE OF THE FIRST PREDETERMINED RATIO OR THE SECOND PREDETERMINED RATIO SUCH THAT 1) THE FIRST AND SECOND ABSORBERS EXHIBIT DIFFERENT INTENSITIES OF ABSORBANCE OF A PREDETERMINED WAVELENGTH, AND 2) AN OPTICALLY DETECTABLE MARK FORMED IN THE FIRST LAYER EXHIBITS A DIFFERENT CONTRAST THAN AN OPTICALLY DETECTABLE MARK FORMED IN THE SECOND LAYER

FIG. 2

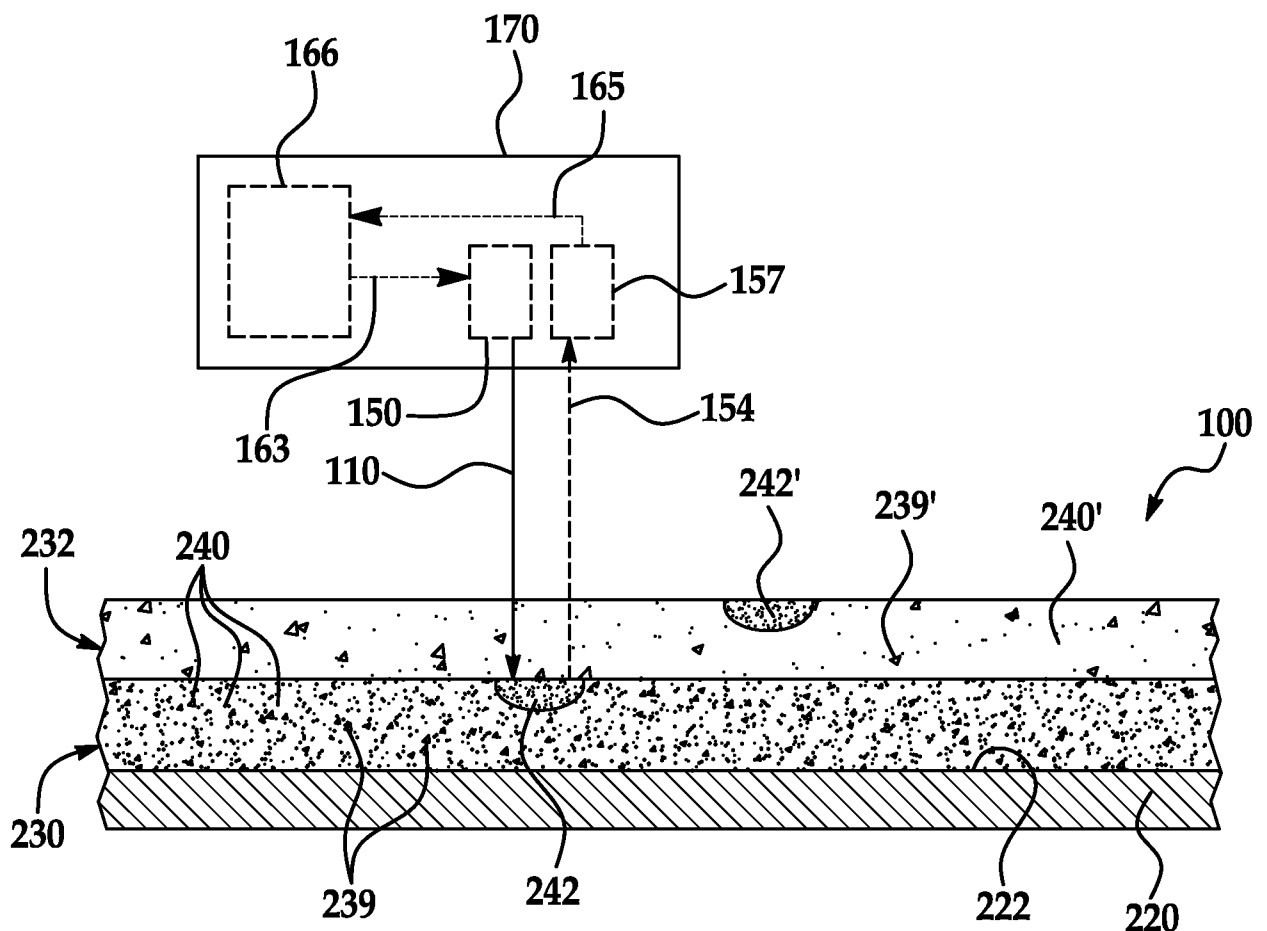


FIG. 4

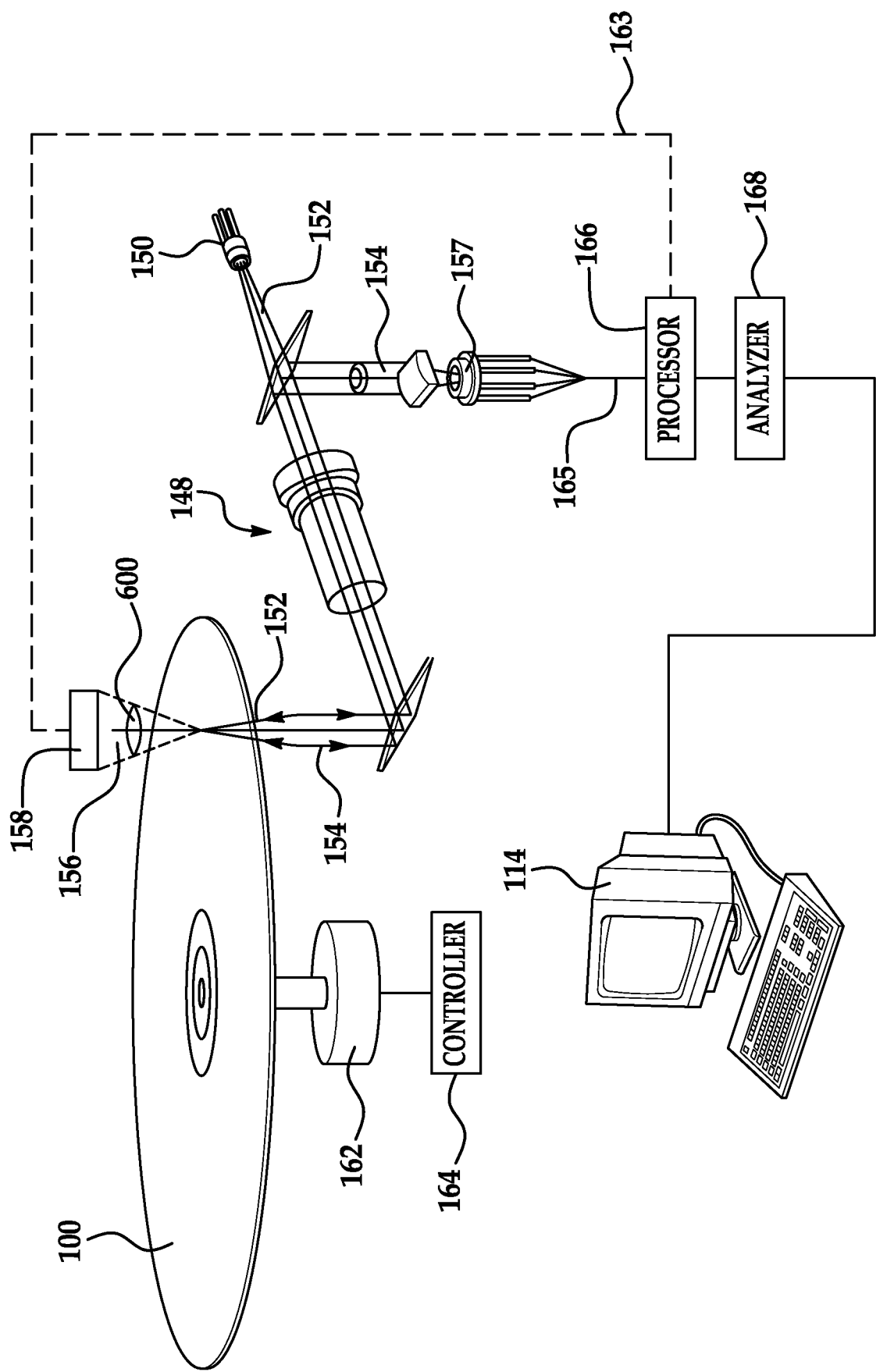


FIG. 3

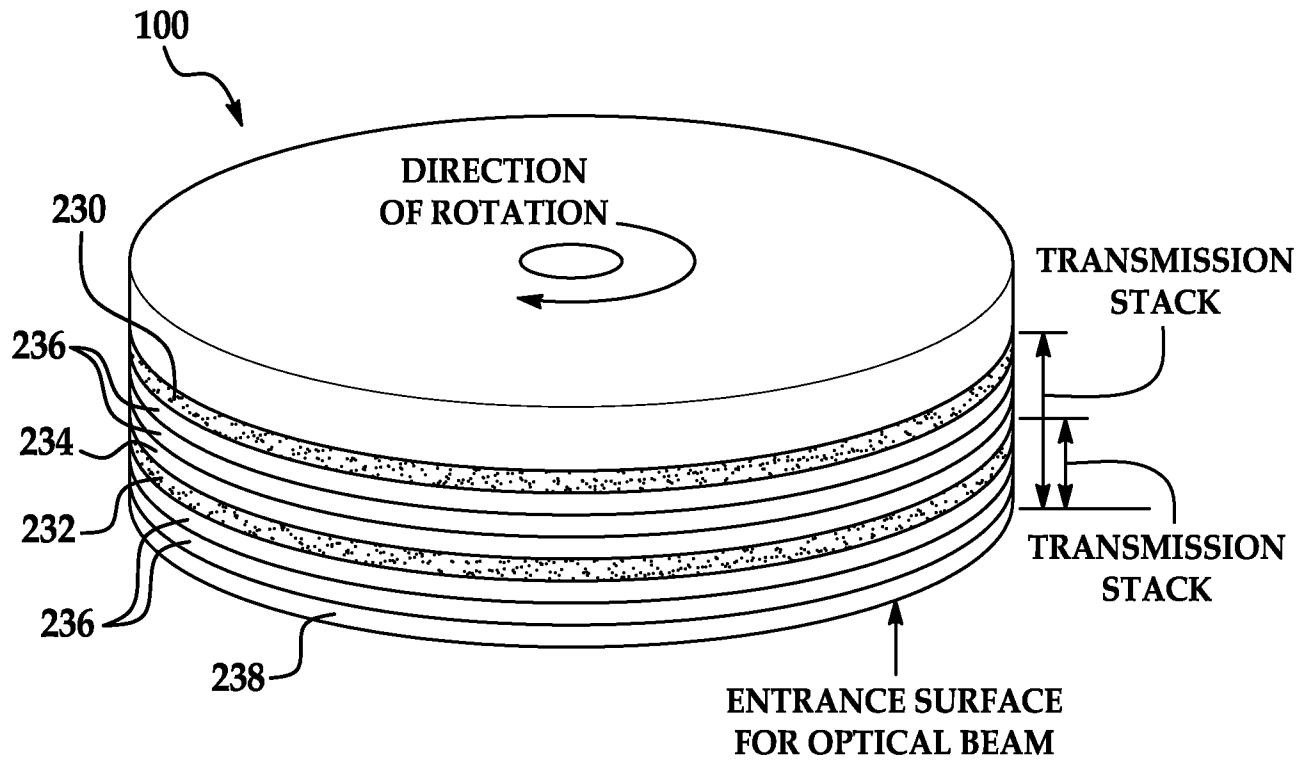


FIG. 5

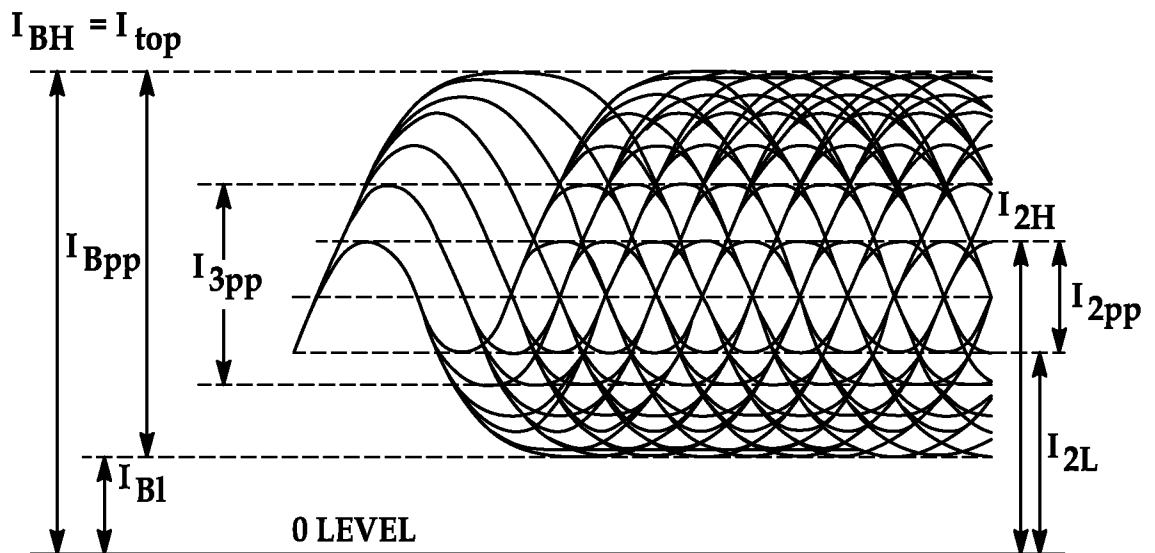


FIG. 6

A. CLASSIFICATION OF SUBJECT MATTER***B41M 5/26(2006.01)i, G11B 7/24(2006.01)i, C07D 487/22(2006.01)i, G03C 1/00(2006.01)i***

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 : B41M, G11B, C07D, G03C1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility Models and applications for Utility Models since 1975

Japanese Utility Models and applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO internal)

"optical", "data", "record", "storage", "medium", "media", "absorb", "dye", "contrast", "multi", "layer"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007-0179057 A1 (GORE) 02 August 2007. See abstract; Figures 1 and 2; Claims 1 - 19.	1-3,6-10,14-22
A	US 5640382 A (FLORCZAK et al.) 17 June 1997. See abstract; Figures 1 - 4; Claims 1-26.	1-3,6-10,14-22
A	KR 10-2005-0035145 A (HEWLETT-PACKARD COMPANY) 15 April 2005. See abstract; Claims 1 - 24; Figures 1 - 3.	1-3,6-10,14-22
A	KR 10-2005-0067107 A (GENERAL ELECTRIC COMPANY & FLEXPLAY TECHNOLOGIES, INC.) 30 June 2005. See abstract; Claims 1 - 19; Figures 1 - 5.	1-3,6-10,14-22
A	KR 10-2006-0037357 A (GENERAL ELECTRIC COMPANY) 03 May 2006. See abstract; Claims 1 - 15; Figures 1, 4 - 8.	1-3,6-10,14-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

08 JANUARY 2009 (08.01.2009)

Date of mailing of the international search report

08 JANUARY 2009 (08.01.2009)

Name and mailing address of the ISA/KR

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gu, Daejeon 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2008/060138

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		WO 2005-010872 A1	03.02.2005

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2008/060138**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4, 5, 11-13, 23-25
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.